

The chief difficulty of the comparison is that of protecting the iron wire from alteration when it is maintained at a red heat for some time. The following Table, II, gives some observations selected at random from a long series in which the zero variation of the iron did not exceed 0·05 per cent. The observations were mostly taken on different days; and the resistances observed at the air temperature in the intervals show the direction in which the correction for zero variation should be applied, but not its amount. It is noteworthy that in all cases the correction for this would tend to reduce the small differences between the formula (*e*) and the observations. As it is, the mean difference is only 0°·1 C.

It does not appear that any other equally simple and convenient formula could be found representing the observations equally well.

Treating the observations on the comparison of two platinum wires in precisely the same way, we shall find for the values of the constants, assuming  $\alpha\beta$  as before for the standard wire—

$$\left. \begin{array}{ll} \text{Standard wire } \alpha = 0 \cdot 0034259. & \beta = 0 \cdot 0015290 \\ \text{Compared wire } \alpha' = 0 \cdot 0033332. & \beta' = 0 \cdot 0015256 \end{array} \right\}$$

so that the values of  $\beta$  are almost identical.

If  $\beta = \beta'$  we have the relation between the resistances at the same temperature

$$\frac{dR}{dt} / \frac{dR'}{dt} = \frac{\alpha R}{\alpha' R'}, \text{ or } \frac{\log R}{\log R'} = \frac{\alpha}{\alpha'}.$$

It is intended to continue the experiments at higher temperatures, and to apply the platinum thermometer to other investigations.

“The Determination of Organic Matter in Air.” By Professor THOS. CARNELLEY, D.Sc., and Wm. MACKIE, M.A., University College, Dundee. Communicated by Sir H. E. ROSCOE, F.R.S. Received June 10. Read June 10, 1886.

The only methods hitherto proposed for determining the amount of organic matter in air are the two devised by the late Dr. Angus Smith (“Air and Rain”). According to the first of these methods, a definite quantity of the air to be examined is slowly bubbled through a dilute solution of potassium permanganate of known strength until it is fully or considerably bleached, and in the latter case the amount of undecomposed permanganate determined by oxalic acid. In the second method a known volume of air is bubbled through distilled water, and the latter examined for free and albuminoid ammonia by Wanklyn and Chapman’s process for water analysis.

These methods are open to one or more of the following objections:—

1. The time required for a single determination is *very considerable*, and necessarily varies with the amount of organic matter present.

2. There is great uncertainty as to whether the organic matter has been fully absorbed and acted on by the permanganate in the first method, or absorbed by the water in the second.

3. It is difficult to determine the exact point of full bleaching, or to estimate by oxalic acid very small degrees of partial bleaching.

4. The methods are inapplicable (chiefly on the score of time and of the extent and complication of the apparatus required) in circumstances and places where such determinations are most desirable. Analyses, especially by the second method, cannot be completed on the spot, except in very rare cases, so that unless a large quantity of apparatus be taken, several consecutive determinations in a series of buildings or rooms is impossible (*cf.* De Chaumont, 'Roy. Soc. Proc.,' vol. 23, 1875).

5. The results obtained by the method proposed below show that very considerable variations in the organic matter are sometimes liable to occur within the period of determination required by Dr. Angus Smith's method.

By the new process, which it is the object of the present paper to describe, the above difficulties are in a great measure overcome. The special advantages we claim for it are:—(1.) Rapidity and simplicity of execution. (2.) A higher probability, though not absolute certainty, that the organic matter is fully absorbed. (3.) A more general applicability.

The *principle of the process* is the same as that of Angus Smith's first method, viz., reduction of potassium permanganate. It differs, however, from Smith's method, more particularly in the mode of estimating the amount of reduction. This consists in determining *colorimetrically*, by comparison with a standard, the *fractional* bleaching effected in a given volume of air.

*Method.*—The solution of permanganate used is of  $\frac{N}{1000}$  strength, of which 1 c.c. = 0.008 mgrm. of oxygen = 0.0000056 litre of oxygen at 0° and 760 mm. It is usually kept of  $\frac{N}{10}$  strength, and diluted as required, about 50 c.c. of dilute sulphuric acid (1 to 6) being added to each litre of the weak solution.

For the collection of the samples of air large well-stoppered jars of about 3.5 litres capacity are used. The jars are first rinsed out with a little standard permanganate, and when not in use some of the solution is always left in them, so as to ensure complete cleanliness from any reducing substance. Before use the jars are drained, and the

sample of air collected by pumping out the contained air with a small bellows, and allowing the air to be examined to flow in. 50 c.c. of the standard permanganate are next run into the jar, which is then tightly stoppered and well shaken up for at least five minutes. 25 c.c. of the permanganate are afterwards withdrawn by a pipette and placed in a glass cylinder holding about 200 c.c., 25 c.c. of the standard solution being placed in a similar cylinder for comparison. Both are next diluted up to about 150 c.c. with distilled water, and allowed to stand for ten minutes, after which the tints in the two cylinders are compared. Standard solution is then run in from a burette, until the tints in both cylinders are of the same intensity; usually from  $\frac{1}{2}$  to 6 c.c. are required.

The amount of solution added from the burette is a measure of the bleaching effected by the known volume of air on half the permanganate employed. This multiplied by 2 gives the total bleaching.

The results may be expressed either in terms of the number of c.c. of the  $\frac{N}{1000}$  bleached by 1 litre of air, or, as we prefer, by the number of volumes of oxygen required to oxidise the organic matter in, say, 1,000,000 volumes of air; *e.g.*, 25 c.c. of solution from a 3.5 litre jar, in which 50 c.c. had been used, required 3 c.c. of the permanganate to bring it up to the standard, or the whole 50 c.c. would have required  $3 \times 2 = 6$  c.c. This represents the number of c.c. of standard permanganate bleached by  $3500 - 50 = 3450$  c.c. of air; consequently  $\frac{6}{3.45} = 1.74$  c.c. is the bleaching effected by 1 litre of air. But 1 c.c. of  $\text{KMnO}_4 = 0.0000056$  litre of oxygen;  $\therefore 1.74$  c.c.  $\text{KMnO}_4 = 0.0000056 \times 1.74 = 0.0000097$  litre of oxygen is required to oxidise the organic matter in 1 litre of air, or 9.7 volumes of oxygen to oxidise the organic matter in 1,000,000 volumes of air.

Correction for temperature was not considered necessary, as it falls within the limits of experimental error. It requires about twenty minutes to collect the samples and complete the analysis. Scrupulous cleanliness is, of course, necessary in all the operations.

We have examined many hundreds of samples of air by this method, and in this large experience of it have found it to be a very convenient and ready process. We believe it to be as accurate as is possible in the present state of the knowledge of this subject. Duplicate analyses of the same air give very concordant results, as evidenced by the examples given below. We are nevertheless fully conscious that objections may be taken to the method on the following grounds:—(1.) That it does not directly estimate the organic matter, but only measures the amount of oxygen required to oxidise either the whole, or more probably only a portion of it. (2.) That the permanganate acts upon various matters in the air, besides the organic matter,

such as sulphuretted hydrogen, nitrous acid, sulphurous acid, &c. (3.) That the organic matter in air is of various kinds, and that consequently the permanganate will most probably be selective in its action. Our knowledge on this point, however, is so defective that no definite conclusion is possible in regard to it. (4.) There is no satisfactory means of checking the results, the only method being to make duplicate determinations of the same air. This test, such as it is, the method stands extremely well, as will be seen from the results given below, which are taken quite promiscuously from a large number of examples:—

Organic Matter.

	Vol. of O required to oxidise the O.M. in 1,000,000 vols. of air.			
	1st Determi- nation.	2nd Determi- nation.	Mean.	
Outside air (Dundee)	9·0	8·9	8·95	Immediately after rain.
" "	12·0	11·5	11·85	No rain during day.
" "	10·0	10·2	10·1	Heavy rain, with wind.
" "	8·6	8·1	8·35	Rain shortly before.
" (Perth) ..	2·0	1·6	1·8	Strong wind and rain.
" "	2·0	1·5	1·75	Strong wind, rain at in- tervals.
" "	2·4	2·0	2·2	Storm shortly before.
" "	4·8	4·6	4·7	Fine.
Class room (Dundee)	10·5	8·8	9·65	Unoccupied, but just after dusting.
" (Perth) ..	7·6	7·8	7·7	29 present for one hour.
" "	4·0	5·0	4·5	31 " " "
Small room . . . . .	11·9	11·4	11·65	Unoccupied, but " with two gas jets burning for 15 minutes.
" . . . . .	12·9	13·0	12·95	With one person and one gas jet for 20 minutes.
" . . . . .	17·2	17·0	17·1	Ditto after one hour and 40 minutes.
" . . . . .	20·0	20·5	20·25	Ditto on another occasion.

(5.) The uncertainty that the permanganate exerts its full action in a cold acid solution of such dilution as that recommended above. The method, however, does not claim to give absolute, but only relative results.

In the general lack of better methods we trust that the modification of the permanganate process we have described will be found of great value, on account of its extreme simplicity and rapidity of execution,

and as giving under the circumstances the greatest attainable accuracy. From our large experience of it, under a great variety of conditions, we believe that, notwithstanding its more or less liability to some or all of the above objections, the method gives results which are perfectly reliable for purposes of comparison.

*Conclusions.*—The following conclusions are deduced from a large number of analyses. The individual data are usually the mean of two duplicate determinations.

(1.) The quantity of organic matter in outside air varies considerably, within certain limits, from day to day, and from hour to hour on the same day.

Variations from day to day are subject to the conditions of the weather.

(a.) It has been found somewhat less immediately after or during rain or snow, thus:—

	No rain or snow.			
	No. of cases.	Lowest.	Highest.	Average.
Organic matter (O required per 1,000,000 vols. of air) . . . . .	19	1·6	15·8	7·9
Carbonic acid (per 10,000 vols. of air) . . . . .	15	2·2	5·4	3·86

	Just after or during rain or snow.			
	No. of cases.	Lowest.	Highest.	Average.
Organic matter (O required per 1,000,000 vols. of air) . . . . .	19	1·8	13·3	7·3
Carbonic acid (per 10,000 vols. of air) . . . . .	11	2·4	5·6	3·95

(b.) The highest results of all were obtained on foggy nights, *e.g.*, 15·7, 17·0. High results were also obtained during a slight drizzling rain, accompanied by mist.

(2.) A close connexion is observed between the amount of organic matter present in air and the combustion of coal. It is lowest in the middle of the night, rather higher in the morning, and considerably

higher in the middle of the day, and higher still towards evening, after which it decreases thus:—

	Night, 8 P.M.—5 A.M.			
	No. of cases.	Lowest.	Highest.	Mean.
Organic matter (O required per 1,000,000 vols. of air) .....	9	2·2	6·7	3·9
Carbonic acid (per 10,000 vols. of air).....	9	3·0	5·6	4·1

	Morning 5 A.M.—10 A.M.			
	No. of cases.	Lowest.	Highest.	Mean.
Organic matter (O required per 1,000,000 vols. of air) .....	4	3·2	6·5	4·9
Carbonic acid (per 10,000 vols. of air).....	9	1·8	4·1	2·9

	Mid-day 10 A.M.—3 P.M.			
	No. of cases.	Lowest.	Highest.	Mean.
Organic matter (O required per 1,000,000 vols. of air) .....	12	1·6	15·7	7·9
Carbonic acid (per 10,000 vols. of air).....	14	2·2	4·9	3·4

	Evening 3 P.M.—8 P.M.			
	No. of cases.	Lowest.	Highest.	Mean.
Organic matter (O required per 1,000,000 vols. of air) .....	25	2·6	16·2	9·1
Carbonic acid (per 10,000 vols. of air).....	20	1·9	5·3	3·5

The above results refer only to ordinary week days, and do not include Saturday and Sunday, which are not normal days in a large town. On several occasions an important decrease was noted towards the noon of Saturday, no doubt due to the stoppage of the boiler fires at the mills and factories. This is shown by the following numbers, which include all the cases observed :—

1885, November 7th.		November 21st.		November 28th.	
Time.	Organic matter.	Time.	Organic matter.	Time.	Organic matter.
10·30 A.M.	8·9	11·30 A.M.	12·7	10·30 A.M.	10·2
12·15 P.M.	8·1	1·30 P.M.	10·6	12·15 A.M.	8·3
1·15 P.M.	8·3	—	—	—	—

A relation to the products of the imperfect combustion of coal is also indicated by the much higher averages obtained for outside air in the centre of Dundee, as compared with the suburbs and with Perth, thus :—

	Dundee (town).			
	No. of cases.	Lowest.	Highest.	Mean.
Organic matter (O required per 1,000,000 vols. of air) . . . . .	46	1·7	16·8	8·9
Carbonic acid (per 10,000 vols. of air) . . . . .	32	2·2	5·6	3·9

	Dundee (suburbs).			
	No. of cases.	Lowest.	Highest.	Mean.
Organic matter (O required per 1,000,000 vols. of air) . . . . .	10	0	5·6	2·8
Carbonic acid (per 10,000 vols. of air) . . . . .	5	1·7	3·5	2·8

	Perth (outskirts).			
	No. of cases.	Lowest.	Highest.	Mean.
Organic matter (O required per 1,000,000 vols. of air) .....	5	1·7	4·5	3·1
Carbonic acid (per 10,000 vols. of air).....	3	2·9	3·5	3·1

(3.) A relation of organic matter to carbonic acid in outside air shows, so far as the tabulated results go, a high carbonic acid accompanied by a high organic matter, and *vice versâ*. This, however, is by no means invariably the case, and is in fact only evident on comparing the averages of a large number of cases. To show this all the determinations which have been made in outside air were divided into four groups, according to the quantity of organic matter present, and the averages of the corresponding carbonic acid found, as in the following table :—

Vols. of O required to oxidise the organic matter in 1,000,000 vols. of air.	Average carbonic acid in 10,000 vols. of air.			No. of determinations.
	Lowest.	Highest.	Average.	
0 to 2·5	too small to estimate.	5·6	2·8	20
2·5 to 4·5		4·9	3·0	20
4·5 to 7·0		5·4	3·2	20
7·0 to 15·8		4·9	3·7	20

(4.) The organic matter in outside air has a far wider range of variations than carbonic acid. For whereas the carbonic acid seldom passes beyond the limits of 2 to 6 vols. per 10,000, the organic matter varies from a quantity too small to estimate to as much as will require for oxidation about 16 vols. of oxygen per 1,000,000 vols. of air.

It is also subject to more rapid fluctuation in its value than carbonic acid.

(5.) The combustion of gas does not appreciably increase the amount of organic matter in air. This was proved by burning gas in a small practically air-tight room (which had previously been well ventilated, and the carbonic acid and organic matter determined),



for a certain length of time, and then making a determination of the carbonic acid and organic matter in the air thus vitiated. The following is an example of a number of experiments all giving similar results:—

	CO <sub>2</sub> per 10,000 vols.	Organic matter (vols. of O required per 1,000,000 vols. of air).
Before gas was burnt .....	4·3	10·6
After the gas had been burn- ing 15 minutes.....	11·0	11·8
After the gas had been burn- ing 30 minutes.....	14·8	11·8

Each of these is  
the mean of  
two nearly con-  
cordant experi-  
ments.

The combustion of gas may therefore be considered too perfect to produce any appreciable effect. What result is obtained may safely be set to the credit of sulphurous acid.

The above remarks apply to Dundee gas, which is considered to be exceptionally pure and free from sulphur.

(6.) *Combustion of Oil Lamps.*—The effect of burning oil lamps is much more marked than that of the combustion of gas. This was determined in a manner similar to that in the case of coal-gas, the experiments being carried out in the same practically air-tight room as before. The following will serve as an example:—

	Organic matter (O required per 1,000,000 vols. of air).	
Before burning of oil lamps .....	8·7	Each of these is the mean of two very closely con- cordant de- terminations.
After one lamp had been burning half an hour, the lamp was found to be smoking slightly ..	12·3	
Ditto after one hour, lamp found burning clear ..	14·6	
After the first lamp had been burning one and a half hour, and a second lamp half an hour, the second lamp was found smoking slightly ....	16·7	
Ditto after first lamp had been burning two hours, and the second one hour, both lamps found burning clear .....	18·1	

In all cases the lamps were burning paraffin oil and were turned on as full as possible without smoking.

(7.) *Respiration.*—Respired air gives a higher result than un-respired air at the same time, though much less than was anticipated.

The effect of respiration was determined as follows:—The observer worked in the small air-tight room previously referred to. This was first ventilated with outside air and then closed, and at the end of

definite intervals the carbonic acid and organic matter present in the air of the room were determined, the analyses being made in the room itself so as to avoid opening the door. The room being unprovided with outside light, one gas jet was kept burning during the whole of the experiments, but the effect of this on the organic matter may be neglected, for, as previously shown, the combustion of coal gas does not appreciably increase the amount of organic matter. The results obtained are shown below :—

		Outside air.	After 20 minutes.	After 30 minutes.	After 60 minutes.	After 100 minutes.
1st experiment	{ CO <sub>2</sub>	3·8	11·4	14·8	—	—
	{ O.M.	9·5	12·9	14·8	—	—
2nd experiment	{ CO <sub>2</sub>	..	..	13·1	23·5	28·2
	{ O.M.	..	..	14·2	15·9	17·0
3rd experiment	{ CO <sub>2</sub>	..	..	17·2	24·1	32·1
	{ O.M.	..	..	13·5	15·7	20·3

Here it is seen that the amount of organic matter becomes greater as the period of vitiation increases, but very much less slowly, so that the increase in the quantity of organic matter is by no means proportional to the time. It also increases less rapidly than the carbonic acid.

(8.) An atmosphere which has been entirely at rest for some time is found to contain less organic matter than it did previously. This is not necessarily entirely due to the settling down of the solid organic dust, but is probably due in part to oxidation.

The statement made in 'Nature' (vol. 33, 1886, p. 130), in an article on ventilation, to the effect that the organic matter in respired air increases *pari passu* with, and is therefore estimated by the amount of carbonic acid present, may be true when the average of a large number of determinations is taken, but is certainly very far from being true in individual cases. At any rate the amount of carbonic acid is no certain index of the quantity of organic matter present in an atmosphere (see above). That air in which respiration has gone on for some time gives invariably a higher result than outside air at or about the same time is all that can be confidently affirmed.

It should not be forgotten that the organic matter in air is most probably partly solid and partly gaseous. The solid obeying a different law than diffusion slowly settles down, whilst the gaseous part, unlike carbonic acid, is most likely an unstable compound or compounds, and readily undergoes oxidation. Experiments were made in regard to this, but they did not give decisive results.